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Nuclear Magnetic Resonance Spectroscopy. A Stereospecific $^3J_{CF}$ Coupling in the Low-Temperature ^{13}C Nmr Spectrum of 1,1-Difluorocyclohexane*

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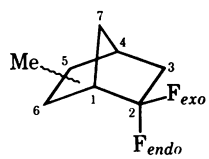
Abstract. The proton-decoupled ^{13}C nmr spectrum of 1,1-difluorocyclohexane has been examined at room temperature and at −90°C. There are only minor changes in the one-bond and two-bond carbon-fluorine scalar coupling constants at the lower temperature; however, the triplet observed for C-3 ($^3J_{CF}$ = 4.7 Hz) collapses to a doublet ($^3J_{CF}$ = 9.5 Hz) at −90°C. It is proposed that only the equatorial fluorine is coupled with the C-3 carbon as the result of operation of a back-lobe orbital interaction.

In a previous publication[1] concerning the ^{13}C proton-decoupled nmr spectra of norbornyl derivatives, a number of methyl-substituted 2,2-difluoronorbornanes (1) were examined. It was found that the C-7 resonance appeared as a doublet with $^3J_{CF}$ on the order of 5 Hz. It was proposed that, in these compounds, carbon-fluorine coupling occurs only with the *endo*-fluorine. This contention was supported by the ^{13}C spectrum of *exo*-2-fluoro-norbornane in which C-7 appeared as a sharp singlet.



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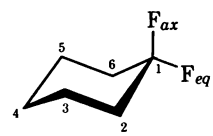

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Similar behavior might be expected for 1,1-difluorocyclohexane (2), provided that the chair-chair interconversion could be halted. The molecular dynamics of 2 are well known,[2] and at −90°C the chair-chair interconversion is slow on the nmr time scale. At room temperature (Fig. 1) the ^{13}C spectrum, with chemical shifts in ppm upfield from internal CS_2 shows triplets at 69.9,[3] ($^1J_{CF}$ = 242 Hz); 165.3, ($^2J_{CF}$ = 24.0 Hz); and 175.5, ($^3J_{CF}$ = 4.7 Hz) assigned to C-1, C-2, and C-3, respectively. The resonance of C-4 appeared as a broad singlet at 173.6 ppm. At −90°C, (Fig. 2), there were only minor (<1 Hz) changes in the $^1J_{CF}$ and $^2J_{CF}$ values; however, the resonance of C-3 now appeared as a doublet, $^3J_{CF}$ = 9.5 Hz. Note that the room-temperature value of $^3J_{CF}$ is half the value observed in the low-temperature limit; we believe, by analogy with the results[1]

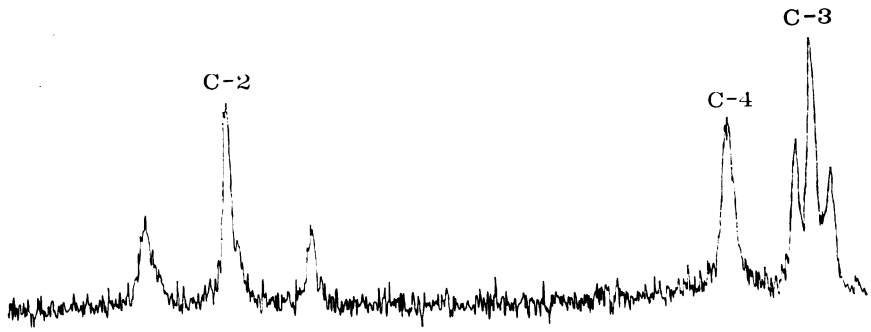

FIG. 1. Proton noise-decoupled ^{13}C spectrum of 1,1-difluorocyclohexane at room temperature. The resonance for C-1 is not shown.

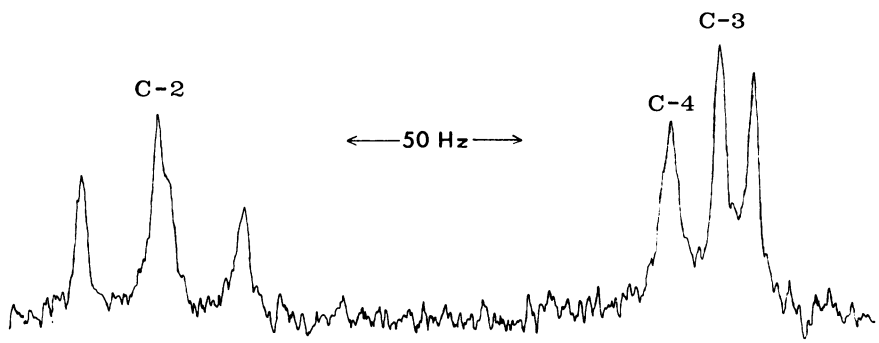

FIG. 2. Proton noise-decoupled ^{13}C spectrum of 1,1-difluorocyclohexane at $-90°C$. The resonance for C-1 is not shown.

observed for **1**, that C-3 is coupled only to the equatorial fluorine. This is consistent with the recent theory,[3,4] involving the coupling between heavy nuclei, that has proposed that there is a significant contribution from through-space interactions (presumably via back-lobe orbital overlap).

It has been proposed[5] that the weak ^{13}C spin-echo Fourier transform (SEFT) spectrum of cyclohexane is due to a high carbon-13 T_1/T_2 ratio, resulting from an extra contribution to the carbon-13 T_2 relaxation time by modulation of the scalar C, H coupling constant associated with the chair–chair interconversion. It was not stated which C, H coupling was being modulated. We believe that the results obtained for **2** are evidence of a significant modulation of $^3J_{CH}$ in cyclohexane and to a short carbon-13 T_2 value. We would predict a similarly weak spin-echo Fourier transform spectrum for perfluorocyclohexane.

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[2] Spassov, S. L., D. L. Griffith, E. S. Glazer, K. Nagarjan, and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 88 (1967).

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[5] Allerhand, A. and D. W. Cochran, *J. Amer. Chem. Soc.*, **92**, 4482 (1970).